COMPRESSIBILITIES, HYDRATION AND ACOUSTIC PROPERTIES OF AQUEOUS SOLUTIONS OF SOME METALLIC SULPHATES

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ABSTRACT Using a fixed path interferometer, ultrasonic velocities have been determined at a frequency of about 1·4 Mc/sec and hence adiabatic and apparent molar compressibilities, acoustic impedance, molar sound velocities and hydration numbers have been calculated in the case of aqueous solutions of sulphates of nine metals at a good number of concentrations upto 3 moles and at the temperature of 28°C. The velocity-variation with concentration, adiabatic compressibility-variation with concentration are found to show a dependence on the atomic weight and the radius of the metallic ion respectively. The apparent molar compressibility, the acoustic impedance and the molar sound velocity are found to vary linearly with square root of concentration, concentration and molar fraction of the solute respectively, and the gradients of the straight lines of these three properties are found to exhibit a general dependence on the molecular weight of the salt. The adiabatic compressibility variation with concentration is observed to be dependent inversely on hydration numbers.

INTRODUCTION

The study of the compressibilities and other related properties of aqueous solutions of salts has proved to be very useful in obtaining information regarding the state of affairs that obtain in a solution. A good amount of work has been recently done in this field by different workers (Subrahmanyam, *et al.* 1960). An examination of the literature on the subject reveals however that the work is not extensive and the results of the different authors are contradictory in certain aspects. As an example it is found that the nature of dependence of the ultrasonic velocities and compressibilities on concentration are ascribed to different factors like the atomic weight of the metallic ion, the ionic radius of the metallic ion, molecular weight of the salt, ionic strength etc. Such an ambiguity is probably because certain salts show dependence of their velocity or compressibility variation on atomic weight of the metallic ion and certain other salts on the ionic radius or on the molecular weight of the salt.

The present paper reports results in ultrasonic velocity, the molar sound velocity, the adiabatic and apparent molar compressibilities and the acoustic impedence in aqueous solutions of 9 metallic sulphates, and the different properties

have been discussed in regard to their variation with concentration as dependent on one or the other of the factors suggested above.

EXPERIMENTAL

A fixed path interferometer (Rao and Rao, 1957) working at a frequency of 1.4 Mc/sec has been employed for the determination of ultrasonic velocities. Though this method involves the velocity determination by altering the frequency of the ultrasonic wave around 1.4 Mc/sec. (which is the fundamental frequency of the crystal) the possibility of dispersion can be ignored in view of the very little changes in the frequency of the order of 0.3 Mc/sec. The other related properties are calculated from the velocities by means of the following relations :

$$\beta = \frac{1}{v^2\rho} \qquad \ldots (1)$$

Where β is the adiabatic compressibility v is the velocity and ρ the density of the solution.

$$\phi = \frac{1000\beta}{C} - \frac{\beta_1}{\rho_1}\left[\frac{1000\rho}{C} - M_2\right] \qquad \ldots (2)$$

ϕ is the apparent molar compressibility

where β and ρ are the compressibility and density of the solution at the concentration C and β_1 and ρ_1 are those of the pure solvent and M_2 the molecular weight of the solute.

$$Z = Pv \qquad \ldots (3)$$

where Z is the specific acoustic impedance.

$$R = \frac{\bar{M}}{\rho} v^{1/3} \qquad \ldots (4)$$

where R is the molar sound velocity, M is average molecular weight calculated from the relation,

$$\bar{M} = \frac{n_1M_1 + n_2M_2}{n_1 + n_2}$$

where n_1 is the number of gram moles of the solute, M_1 molecular weight of the solute, n_2 the number of gram moles of the solvent, M_2 molecular weight of the solvent.

$$\lim_{C\to 0} \phi = -\beta_1 V_n \qquad \ldots (5)$$

where V_n is the volume of primary water of hydration for mole of the electrolyte. The limiting value of $\underset{c\to 0}{\phi}$ is obtained by extrapolating ϕ versus $\sqrt{C}$ graph to zero concentration. V_n is then divided by molar volume of the solvent molecules in the primary hydration sheath which gives primary hydration number.

RESULTS AND DISCUSSIONS

Ultrasonic velocity : For all salts chosen in this study the ultrasonic velocity is found to increase with increasing concentration, relatively slower at lower concentrations, say, up to 0 5 mole, and more rapidly beyond that concentration. The curves indicate that the variation approximates to being linear between 0.5 and 2 or 2 5 moles. The gradients of the approximately straight portions of the velcoity curves are calculated. It is rather interesting to find that in the case of six sulphates of the metals, lithium, magnesium, iron (ic), nickel, cobalt and cadmium out of the nine taken up the gradients are found to decrease with increasing atomic weight of the metalic ion. Since the sulphate ion is common for all these salts, the decrease in the gradients (the gradient indicating the rate of variation of velocity with concentration) must reasonably be attributed to the increase in the atomic weights of the metallic ions. A logical extension of this idea means that for salts with metallic ions of higher and higher atomic weights,

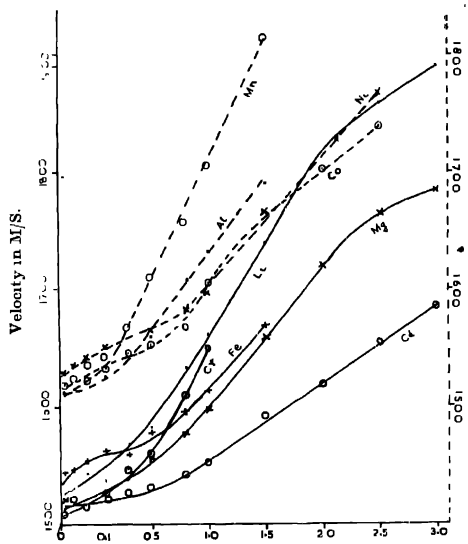

Fig 1. Variation of ultrasonic velocity with concentration.

the rate of variation of velocity goes on decreasing and for salts with heavy metallic ions the velocity may decrease with increasing concentration. This expectation is corroborated by the results in certain heavy metallic salts reported earlier by the authors, wherein it was shown that in the case of six heavy metallic salts the velocity decreased with concentration.

Adiabatic compressibility · The adiabatic compressibility has decreased with concentration for all salts. Between 0 1 and 2 moles the rate of variation approximates to being linear the gradient being very nearly the same for a majority of the salts worked. When an attempt is made to study the dependence of the variation of β with concentration on the ionic radius of the metallic ion it is found that in the case of the salts of the metals manganese, chromium, iron(ic), nickel, cobalt, cadmium which are in the order of increasing ionic radius of the metal

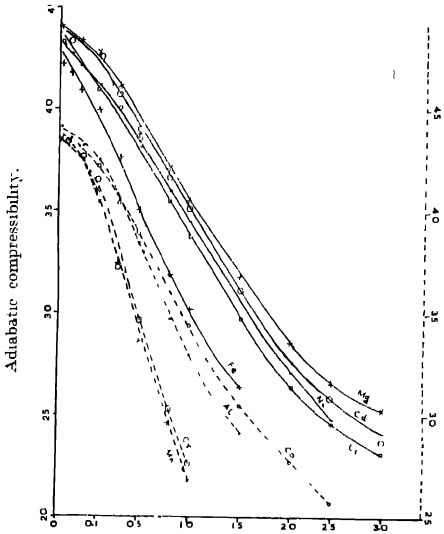

Fig. 2. Variation of adiabatic compressibilities with concentration

ion, the β concentration curves are displaced up, which means that at corresponding concentrations the β values increase for salts with metallic ions of increasing radius. This contradicts the findings of an earlier author (Marks, 1959) where in the reverse dependence was reported. But as his result has been confined to quite a few salts the correctness of the result is open to question.

Apparent molar compressibility :—The apparent molar compressibility ϕ is found to increase linearly with $\sqrt{C}$ only at higher concentrations, say, beyond 0.5 mole and not at the lower concentrations This result is in conformity with similar findings of the authors (Satyanarayanamurty and Krishnamurty, 1962) in the case of nitrate solutions. An attempt is made to study the dependence of the gradients of the ϕ to $\sqrt{C}$ straight lines on the molecular weights of the salts. A similar study was done in the case of the salts of the nitrates as reported in an earlier publication (Satyanarayanamurty and Krishnamurty, 1962) wherein

a general, though not exactly linear, dependence between the gradients of ϕ to $\sqrt{C}$ straight lines and molecular weights was found in the case of 10 salts. The molecular weights of the salts of the present investigation and their respective gradients are also found to exhibit the general dependence.

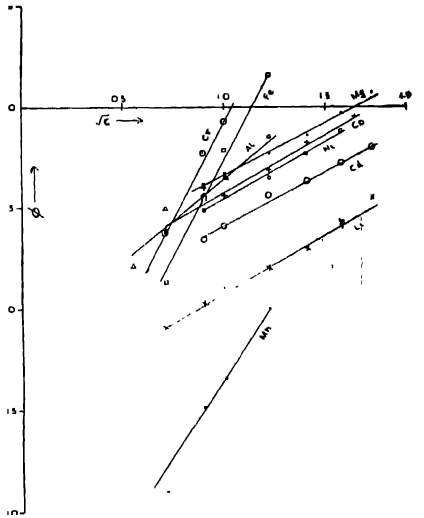

Fig. 3 Variation of "ϕ" with "$\sqrt{C}$

Acoustic impedence The acoustic impedence Z depends linearly on the concentration for all the salts taken up here as can be seen from Fig. 4. This confirms Marks findings in the case of some salt solutions. It is also interesting to observe the gradients of the $Z-C$ straight lines show an increase with increasing molecular weight for five salts namely those of Li, Cd, Al, iron(ic) and Cr. Also in the case of other salts of the present investigation there is a general dependence between the two, as for instance, the values of the gradients are almost the same for salts of Cd, Ni and Co whose molecular weights are also almost the same.

However according to equation proposed by Prakash and Srivastava (1958), $(\rho/\beta)^{1/4}$ that is $Z^{\frac{1}{2}}$, is expected to be linearly dependent on the Ionic strength μ and the gradients for various salts have to be the same. But when we have plotted $\sqrt{z}$ verses μ (Fig. 5) for the salts of the present study, it can be seen that only at lower ionic strengths the relation can be called as being reasonbly linear. Also the gradients are found to be by no means the same for all salts.

Molar sound velocity R . As can be seen from Figs. 6 and 7 the molar sound velocity R is found to vary linearly with the molar fraction of the solute

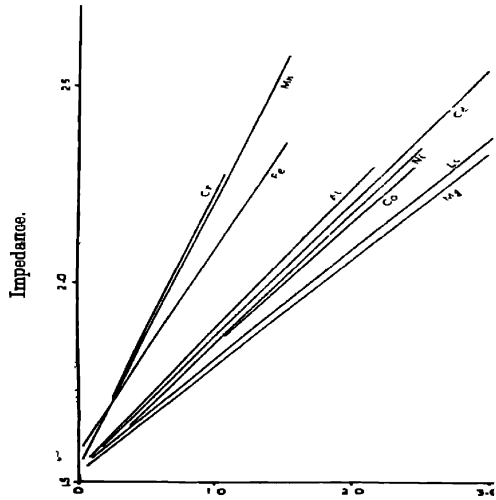

Fig. 4. Variation of acoustic impedance with concentration.

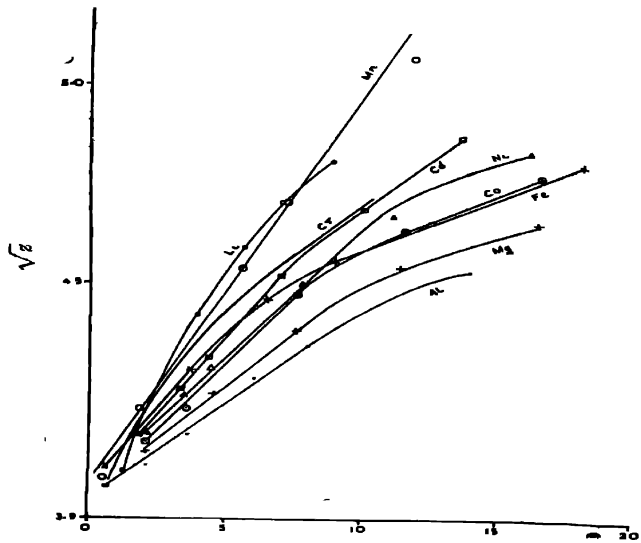

Fig., 5. Variation of "$\sqrt{z}$" with ionic strength.

as is already suggested by earlier authors (Padmini and Rao, 1960). The gradients of these straight lines (see Table 1) are found to show a general dependence on

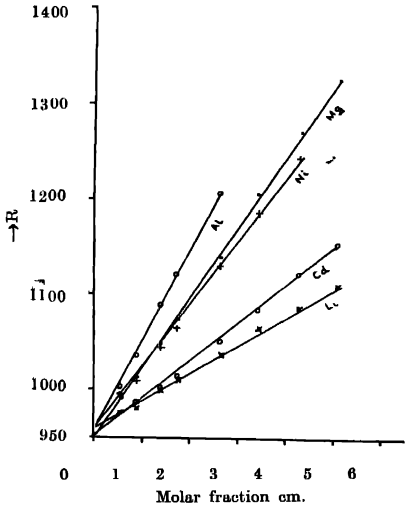

Fig. 6. Variation of molar sound velocity with molar fraction.

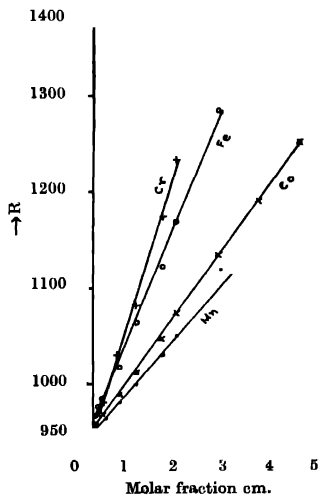

Fig. 7. Variation of molar sound velocity with molar fraction.

TABLE I

	Salt sulphate	Molecular weight	Atomic weight of the metallic ion	Radius of the metallic ion	Gradient of V versus C graph	Gradients $\phi - \sqrt{C}$ graph	Gradients of Z-C lines $\times 10^3$	Gradient of cm $-$R lines	φ $C \rightarrow 0$	Hydration numbers
1	Lithium $Li_2 So_4 H_2O$.	127.96	6 94	0.6	166 6	5 8	27 65	29 36	-15	18.68
2.	Magnesium $MgSO_4$. $7H_2O$.	246 5	24.32	0 65	112 7	5 16	26 83	73 98	-8.5	10 59
3.	Cadmium $Cd\ SO_4$, $7H_2O$	280 59	112 41	0.97	65 43	5 4	33 43	39 70	-11.3	14 08
4.	Nickel $NiSO_4$. $7H_2O$	280.71	58 71	0 69	108	5 72	32 87	66 01	-10.2	12.71
5.	Cobalt $CoSO_4$, $7H_2O$.	281	58 94	0.72	80	5 8	31 18	69 13	-10	12.46
6.	Aluminium $Al_2(SO)_3$	342.2	26.98	0.54	105.9	8 4	35 16	95 66	-11.8	14 70
7.	Mangannic $Mn_2(SO_4)_3$.	398.1	54 93	0.51	204	15 67	66.94	8.06	-29	36.13
8.	Ferric $Fe_2(SO_4)_3$ $9HO_2$.	562	55.85	0 67	106	18 20	50 94	93.42	-21	26.16
9.	Chromium $Cr_3\ (SO_4)_3$, $18H_2O$.	716.5	52.01	0 65	175	18.75	68.95	157 40	$-19\ 6$	24 42

the molecular weight of the salt by way of increasing for salts with increasing molecular weights. It can be seen that the gradients and the molecular weights increase for the salts of Li, Cd Ni, Co, Fe, Cr.

It has been so far pointed out that the variation of the apparent molar compressibility, acoustic impedence, and the molar sound velocity with concentration shows a general but definite dependence on the molecular weight of the salt. The authors therefore suggest that the important properties of an aqueous solution dependent to a larger extent on the molecular weight of the solute rather than other factors like weight, radius and valence of the cation.

Hydration numbers : A few earlier workers have commented on the effect of hydration on β. One suggestion was that the dependence of variation of β with concentration on cationic radius is influenced by hydration. In the present case, it is found that for salts with decreasing hydration numbers the corresponding β-c curves are displaced up. It happens in the case of the salts of Mn, Fe, Al., Ni, Co, Mg. This means that at any chosen concentration the β depends inversely on hydration number.

It has already been noted that the $\beta - c$ curves are displaced up for salts of metals with increasing cationic radius. This result coupled with the inverse dependence $\beta - c$ variation and hydration numbers implies that as the cationic radius increases the hydration number of the salt decreases. This corroborated by the fact (Suryanarayana, 1962) that in the case of monovalent ions that the hydration numbers decrease in the order of $Li > Na > K > Rb > Cs$, and in the case of divalent cations in the order $Mg^{++} > Ca^{++} > Sr^{++} > Ba^{++}$, in both the cases the metals being put in the order of their increasing ionic radius.

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